

(19) Japan Patent Office (JP)
(12) KOKAI TOKKYO KOHO (A)
(11) Unexamined Patent Application: Showa 64-24849 (Heisei 1-24849)
(43) Publication Date: January 26, 1989

(51) Int. Cl. ⁶	Id. Symbol	Office Ref. No.
C 08 L 67/02	LPG	7311-4J
/(C 08 L 67/02		
C 08 L 77:00)		

Examination Request: None

No. of Inventions: 1 (total pages: 4)

(54) Title of the Invention: POLYESTER RESIN COMPOSITION

(21) Application No.: Showa 62-182065

(22) Application Filed: July 21, 1987

(72) Inventor: M. Unno
Address: 1, Uekawanari, Funegoe-cho, Okasaki-shi, Aiji-ken
(72) Inventor: K. Kuwabara
Address: 19-11, Hinanaka-cho, Okasaki-shi, Aiji-ken
(72) Inventor: M. Tokushima
Address: 4-1, Hinanaka-cho, Okasaki-shi, Aiji-ken
(71) Applicant: Nippon Esuteru K. K. (Japan Ester Co., Ltd.)
Address: 4-banchi-1, Hinanaka-cho, Okasaki-shi, Aiji-ken

(74) Patent Representative: Y. Kunidama, patent attorney.

Translated from Japanese by:
Michael J. Sidor & Co., Inc.
527 S. Mitchell Ave.
Arlington Heights, IL 60005
847-259-7697
File No.: MS2610

1. Title of the Invention

POLYESTER RESIN COMPOSITION

2. Patent Claim

(1) A polyester resin composition in which a polyester containing ethylene terephthalate as the main repeating unit contains 50-50,000 ppm aliphatic polyamide, wherein the content of acetaldehyde after melting and holding the composition for 60 s at a temperature of 280°C in a nitrogen atmosphere is 10 ppm or less.

3. Detailed Description of the Invention

Field of Industrial Application

The present invention relates to a polyester resin composition that has a very low content of acetaldehyde (abbreviated as AA below) even after melt molding.

Prior Art Technology

In recent years, polyesters, such as polyethylene terephthalate (abbreviated as PET below), have been widely used for the manufacture of various bottles for beverages and food products and films for packaging food.

However, a problem associated with PET was that it generated AA in melting. PET already contains AA even after polymerization, but the additional amount of AA is generated when PET is melt-molded to obtain bottles and a large amount of AA is contained in the bottles. When beverages are poured into such bottles and stored therein, AA is eluted into the beverages, thereby degrading their taste. Therefore, it is desired to minimize the content of AA in PET.

The conventional method for decreasing the content of AA in PET comprised chipping the melt-polymerized PET, conducting solid-phase polymerization producing PET with the AA content decreased to about 10 ppm, and using this PET for melt molding under molding conditions suppressing the generation of AA.

Problems Addressed by the Invention

Though it is important to decrease the AA content in PET prior to molding by, for example, solid-phase polymerization, the AA content after melt molding is always higher than that before molding and it is very difficult to suppress the AA content in PET after molding to less than 10 ppm.

The AA content (I) in PET after melt molding is the sum of the AA content (II) in PET after melt molding and the amount of A (III) generated in melt molding. Thus,

$$I = II + III.$$

With the conventional methods, I was decreased by decreasing II. By contrast, in accordance with the present invention, I is decreased by decreasing not only II, but also III. In the prior art, an attempt has been made to decrease III by comprehensively studying molding conditions, but I was still very difficult to decrease to less than 10 ppm.

Accordingly, the object of the present invention is to provide a polyester resin composition that has a very low AA content even after melt molding.

Means to Resolve the Problems

The inventors have conducted intensive research to attain this object. The results of this research laid the foundation for the present invention. Thus, the present invention provides a polyester resin composition in which a polyester containing ethylene terephthalate as a main repeating unit contains 50-50,000 ppm aliphatic polyamide, wherein the content of AA after melting and holding the composition for 60 s at a temperature of 280°C in a nitrogen atmosphere is 10 ppm or less.

The present invention will be described below in greater detail.

The polyester used in accordance with the present invention contains ethylene terephthalate. It is preferred that this polyester be obtained by solid-phase polymerization to decrease the AA content therein. A part of the ethylene glycol component may be substituted with other glycols, such as tetramethylene glycol and neopentylene glycol, and a part of the terephthalic acid component can be substituted with an aromatic dicarboxylic acid, such as

isophthalic acid, naphthalenedicarboxylic acid, and diphenyldicarboxylic acid. Furthermore, the polyester in accordance with the present invention may also contain various additives, such as an agent improving heat and oxidation resistance, a UV absorber, and a coloring agent.

Such a polyester can usually be manufactured by a melt polymerization process or a combination of a melt polymerization process and a solid-phase polymerization process. The intrinsic viscosity $[\eta]$ of the polyester is preferably above 0.60, still more preferably above 0.70.

It is imperative for the composition in accordance with the present invention that the polyester contain 50-50,000 ppm of an aliphatic polyamide. When the content of the aliphatic polyamide is less than 50 ppm, the effect of the aliphatic polyamide, that is, the suppression of AA generation in PET, is reduced, which is undesirable. On the other hand, when this content exceeds 50,000 ppm, the blow moldability in molding a bottle from a preform degrades, which is also undesirable.

It is preferred that the aliphatic polyamide be synthesized from a C_{2-20} diamine and a C_{2-20} dicarboxylic acid, or a C_{2-20} aminocarboxylic acid, or a lactam containing at least four carbon atoms per molecule, or be prepared by copolymerization of two or more such components. Furthermore, hydrogen atoms in the aliphatic chain may be substituted with an alkyl group, an alkoxy group, an acyl group, or a halogen atom.

The preferred method for the manufacture of the polyester resin composition in accordance with the present invention of the above-described polyester containing ethylene terephthalate as the main repeating unit (referred to as a polyester below) and aliphatic polyamide comprises using a twin-screw melt-kneading extruder, continuously kneading the polyester and aliphatic polyamide at the prescribed ratio, extruding into a strand, and cutting into chips.

Methods for the manufacture of the composition in accordance with the present invention are obviously not limited to the above-described method.

The polyester resin composition obtained by the above-described method, for example, must have a content of acetaldehyde after melting and holding the composition for 60 s at a temperature of 280°C in a nitrogen atmosphere of 10 ppm or less.

The amount of AA generated from polyesters, in particular from PET, in melting tends to increase with an increase in melting temperature and melting time (retention time). Typically, when polyesters are molded into bottles, the molding temperature is about 280°C (an even higher molding temperature is required when the intrinsic viscosity $[\eta]$ is very high) and the molding cycle is about 30 s. Therefore, the AA content after the polyester resin composition is held in a molten state for 60 s at a temperature of 280°C becomes a measure for the AA content after molding of, for example, a bottle.

Operation

The polyester resin composition in accordance with the present invention is a polyester containing 50-50,000 ppm of aliphatic polyamide uniformly distributed therein. The AA content after melt molding of such a polyester is very small by comparison with 100% polyester containing no aliphatic polyamide.

It is not clear what is the mechanism of such an effect. Apparently, it is due to the presence of amide groups or end groups (amino groups, carboxyl groups) in the aliphatic polyamide chain. In any case, the present invention made it possible to suppress the AA content after molding to less than 10 ppm in polyesters in which such a result was very difficult to obtain if a 100% polyester composition was used, regardless of how accurately the conditions of melt polymerization, solid-phase polymerization, and molding were controlled.

Furthermore, a significant advantage of the invention composition is that the amount of AA generated is very small when the melting and holding temperature is not only 280°C, but also 270°C, 290°C, or 300°C, and the holding time is longer than 60 s, provided that the polyester resin composition in accordance with the present invention and the 100% polyester composition are tested by melting and holding under the same conditions.

Embodiments

The present invention will be explained below in greater detail with reference to its embodiments.

In the embodiments, the melting and holding test and the measurement of AA content were conducted in the following manner.

Melting and Holding Test

A sample, 3 g, vacuum-dried for 3-5 h at a temperature of 120-150°C was placed into a glass tube and the atmosphere inside the tube was replaced with nitrogen. Then, the tube was immersed into an oil bath heated to a temperature of 280°C and allowed to stay there for 60 s. The tube was then taken out of the oil bath and cooled to room temperature.

Measurement of AA Content (water extraction method)

A sample, 2.5 g, was sealed inside a glass tube together with 10 mL of distilled water and extracted for 2 h at a temperature of 160°C followed by cooling to below 5°C. The AA content was measured by gas chromatography. The result was represented in ppm.

The intrinsic viscosity $[\eta]$ was measured at a temperature of 20°C in a mixed solvent containing equal amounts (weight) of phenol and carbon tetrachloride.

Embodiments 1-4 and Comparative Examples 1-3

PET having an AA content of 5.2 ppm and an intrinsic viscosity $[\eta]$ of 0.73, prepared by the usual melt polymerization and solid-phase polymerization method, and poly- ϵ -caprolactam (Nylon 6) were kneaded at ratios shown in Table 1 using a twin-screw melt kneader to give the respective compositions. The extrusion temperature in this process was 275°C and the screw rotation rate was 180 rpm. The obtained compositions were subjected to the melting and holding test and the AA content in the compositions was measured. The results are presented in Table 1.

Table 1

	Nylon 6	AA content (ppm)
Comparative Example 1	0	36
Comparative Example 2	10	28
Embodiment 1	100	9.2
Embodiment 2	1000	7.4
Embodiment 3	10000	6.6
Embodiment 4	30000	6.3
Comparative Example 3	80000	6.2

When the composition of Comparative Example 3 was molded into a bottle, the blow moldability was low and the productivity decreased.

Embodiment 5

A composition was prepared in the same manner as in Embodiment 2, except that polyhexamethylenedipamide (Nylon 6.6) was used instead of Nylon 6. The composition was subjected to the melting and holding test. The AA content was 7.6 ppm.

Effect of the Invention

The embodiment described above shows that the polyester resin compositions in accordance with the present invention have a very low AA content even after melting and holding. Therefore, even after melt molding a bottle, the AA content in the bottle is low. Consequently, the invention composition is perfectly suitable as a resin for bottles, for example, for mineral water and various beverages, including carbonated beverages.

Furthermore, the invention composition is also suitable as a resin for films that are used in direct contact with food products.

Applicant: Nippon Esuteru K. K.

Patent Representative: M. Oyadama.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP; BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.